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Abstract

Development of advanced hydrogen separation membranes in support of hydrogen production processes such as coal gasification and as front end gas purifiers for fuel cell based system is paramount to the successful implementation of a national hydrogen economy. Current generation metallic hydrogen separation membranes are based on Pd-alloys. Although the technology has proven successful, at issue is the high cost of palladium. Evaluation of non-noble metal based dense metallic separation membranes is currently receiving national and international attention. The focus of the reported work was to develop a scaled reactor with a V-Ni-Ti alloy membrane to replace a production Pd-alloy tube-type purification/diffuser system.

Introduction

Hydrogen separation and purification has been identified as a bottleneck in the development of advanced hydrogen fuel technologies. Many techniques for hydrogen separation are in use or are currently being investigated, such as cryogenic separation, pressure swing adsorption, catalytic purification and selective diffusion. As a result of its high hydrogen permeability, good mechanical characteristics and highly catalytic surface, which dissociates hydrogen rapidly, palladium is still the membrane material of choice for many applications. Unfortunately, palladium and its alloys are extremely expensive, roughly twice the cost of gold, making them impractical for large-scale or distributed applications. Therefore, an economically feasible, palladium-based, commercial scale system would require a significantly reduced amount of palladium, which can be accomplished by techniques such as thin palladium membranes supported on porous substrates or highly permeable bulk substrates. However, the high cost of palladium has turned the attention of researchers to palladium-free membrane technologies, such as cermets and ceramics for high-pressure, high-temperature applications.

The current generation of gas purification/separation membranes is based on Pd/Pd-alloy used either independently or in conjunction with porous ceramic supports. While Pd/Pd-alloys have many favorable attributes, the major drawbacks to their industrial use are high cost for Pd, relatively low flux, and that during cycling above and below a critical temperature an irreversible change takes place in the palladium lattice structure which can result in significant damage to the membrane. Palladium coated ceramic membranes offer the potential for extended temperature range operations but suffer from the fatal flaw of “pinhole” short circuit paths. Any “pinholes” in the Pd-catalytic film on the surface of the ceramic substrate will potentially allow contaminant/intermediate species to pass directly through the membrane thus effectively reducing the purification factor of the membrane. Recent efforts in the hydrogen purification/separation membrane community have focused on the development and evaluation of non-palladium based membranes that offer a lower cost, high flux, and highly durable

membranes to replace Pd-based systems. Group 5A metals such as V, Nb, and Ta are currently being evaluated by numerous researchers and show promising results with respect to hydrogen permeability [1-3]. However, these metals suffer from severe hydrogen embrittlement and thus are unacceptable for membranes. Japanese researchers have begun to evaluate alloying additions—Al, Ni, Co, and Mo—to vanadium in hopes decreasing the susceptibility to hydrogen embrittlement [4,5].

The most interesting recent result has been the evaluation of Ni-Ti-Nb alloys for hydrogen permeation [6]. Ni-Ti has long been known as a shape memory alloy but it also possesses good hydrogen solubility and mechanical properties. The major drawback is that hydrogen diffusivity in Ni-Ti is considerably slower than either Pd/Pd-alloy, V, Nb, or Ta. In attempt to enhance the diffusivity, additions of Nb have been made to Ni-Ti alloys and permeation and mechanical stability have been evaluated. The limited study of ternary Nb-Ti-Ni alloy has shown permeation on an order equal to pure Pd and reasonable mechanical stability in hydrogen. Recent work on V-Ti-Ni and Ta-Ti-Ni alloys by the same authors has shown similar results. The permeabilities of the V- and Ta-alloys were not quite as high as either Pd or the previous studied Nb-alloys [7,8]. This was attributed to the inherent greater permeability of bulk Nb in comparison to V and Ta.

The focus of this work is to develop a planar fifth scale reactor and test the characteristics, ease of fabrication, and throughput of this non-prototypic reactor made using a Nb-Ti-Ni membrane.

Developmental Approach

Material Preparation

Materials of interest were prepared by arc melting buttons of approximately 25 grams each in a Centorr System VII arc melter system with a tungsten electrode. Arc melting was performed following evacuation to approximately 10^{-4} Torr and backfilling with argon. The V-Ti-Ni alloys were prepared using 99.7%V, 99.95%Ti, and 99.95% Ni raw materials supplied by Alfa-Aesar. The V-Ni-Ti alloy tested as part of this study contained the following alloy composition—53wt%V, 26wt%Ti, and 21wt%Ni. Characterization of the as-cast microstructure was performed using light optical microscopy on polished and etched samples. Scanning electron microscopy and energy dispersive x-ray spectroscopy—including X-ray dot mapping—using a Hitachi S3600 were performed to characterize the phase structure and elemental distribution. Disks approximately 12mm in diameter and 0.5-0.75mm in thickness were sectioned from the arc melted buttons and prepared via grinding on SiC papers to provide a 1200 grit finish.

Permeation test samples, 19 mm diameter and 0.89 mm thick or disks were electron beam welded into 2.12" diameter Conflat (CF) flanges. Crevices were seal welded using electron beam welding to minimize the effects of virtual leaks. The sample assemblies were placed in a 1" OD vacuum system fabricated with 2.12" CF flanges. Copper gaskets were used to seal the samples.

A 30 cm x 10 cm x 2.5 cm ingot of 51V-28Ti-21Ni was also vacuum arc cast followed by vacuum induction skull melting. The ingot was hot isostatically pressed (HIP) to heal all the internal porosity, Figure 1. This ingot was used to fabricate large scale membrane pieces. The ingot was characterized using optical and scanning electron microscopy. Sheet type membrane material was electrical discharge machined (EMD) to a thickness of nominally 0.25 mm. The sheets were surface ground using SiC papers to remove the EDM recast layer.

Figure 1. As cast and HIP condition of the 51V-28Ti-21Ni ingot used to make 25 μm thick sheets for the permeator.

Initially, e-beam welding was to be used to fabricate the scale reactor. Due to thermal strains and cracking during fabrication test welds, the samples were brazed into the stainless steel support structures. The condition of an as-brazed membrane is shown in Figure 2. The braze process resulted in a rumpled surface. During the surface preparation step of several sheets, through sheet holes were detected. These holes repaired by brazing disks of the alloy to the surface using the same BAu-4 braze alloy.

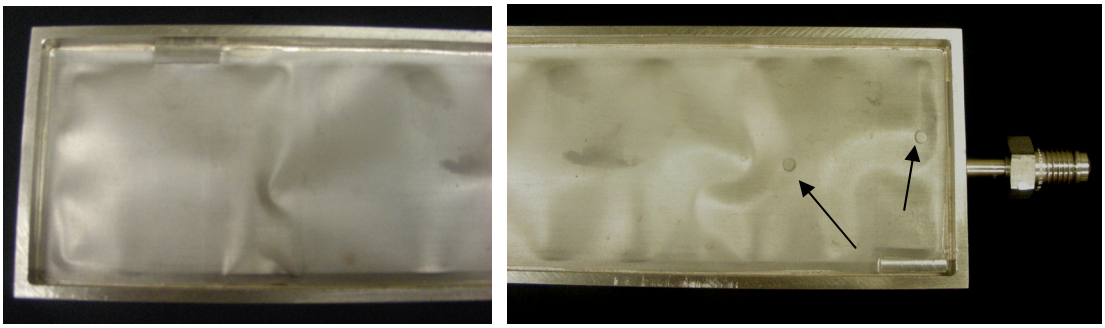


Figure 2. The typical condition of an as-brazed membrane, arrows show braze repaired pores that were not present on the tested membrane.

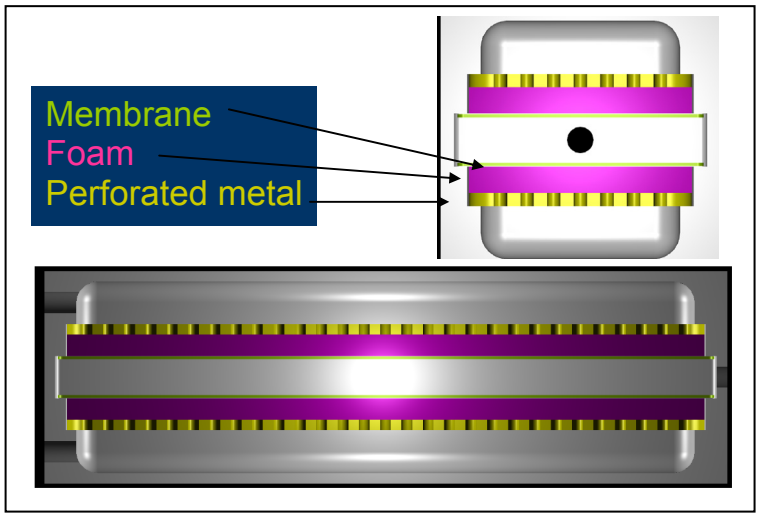
Design Evolution

Several designs were considered from a simple planar circular design, such as that shown in Figure 3, to a multi-port design. The circular design was abandoned due to the relatively low surface area that can be achieved with reasonably sized disks. Flexural strains in large diameter membranes were a determining factor in considering alternative geometries. A rectangular membrane shape was selected to maximize the surface area and be able to make a twentieth scale model, based on membrane surface area, of a production tube type diffuser.

Typical Pd Tube Type Reactor

The baseline reactor that this project is intended to replace is shown in Figure 4. It is contained in an envelop of approximately ten inches in diameter and 20 inches long and is comprised of approximately 780 cm^2 of Pd alloy surface. The Pd tubes are attached to the stainless steel fittings using brazed transition joints that are subsequently welded to stainless steel fittings. The reactors are generally robust, but occasionally there have been joining and fabrication issues and challenges. In addition, the Pd membranes may coke or be poisoned by feed gas contaminants.

(a)



(b)

Figure 3. Possible permeator geometries (a) cylindrical (b) cartoon of proposed system for a 10% scale reactor.

Results and Discussion

Microstructure

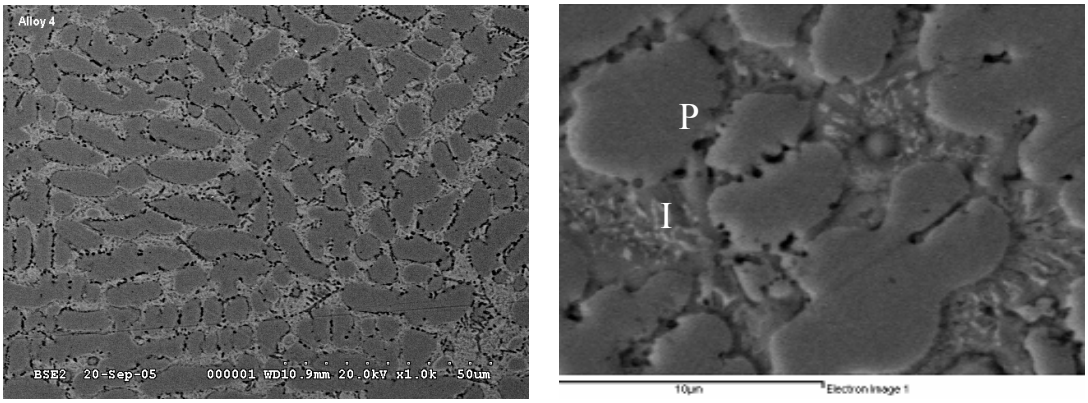
Evaluation of the microstructure of the V-Ti-Ni alloy was performed using scanning electron microscopy combined with x-ray mapping of the element constituents. Previous work on Nb-Ti-Ni alloys being investigated for advanced hydrogen separation membrane use has attributed positive results to microstructures consisting of a large primary $Nb_{83}Ti_{13}Ni_4$ phase surrounded by eutectic (NiTi +NbTiNi); $Nb_{83}Ti_{13}Ni_4$ was postulated to be the high diffusivity phase while the eutectic structure contributes to the lack of susceptibility to hydrogen embrittlement [6]. SEM backscattered and secondary electron micrographs of the V-Ti-Ni alloy display a similar microstructure to the Nb-Ti-Ni alloy with a primary phase surrounded by interdendritic eutectic structure—Figure 5. X-ray mapping of the elemental constituents indicates that the primary phase (P) in the microstructure is high in vanadium. Additionally, the interdendritic (I) eutectic is rich in Ni and Ti. Semi-quantitative chemical analysis of the composition of the vanadium rich primary phase indicates an approximate composition of $V_{75}Ti_{16}Ni_9$.

Baseline Permeation Testing

Measurement of the steady state permeation flux for the V51-Ti28-Ni21 alloy of Figure 6 was conducted and compared to literature data for palladium membranes. The testing was conducted under sub-atmospheric pressures but at values typically used at the Savannah River Site for hydrogen isotope purification. A typical raw data curve for sample D2 (V51-Ti28-Ni21)

is shown in Fig. 5. The measured permeability was 2.1 x 10^{-9} mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$ compared to Pd flux of 2 x 10^{-8} mol H_2 m^{-1} s^{-1} $Pa^{-1/2}$, or within a decade. Consequently, with reduced raw materials cost it was determined that this material could provide a viable alternative to Pd alloys.

Figure 4. Typical jacketed Pd alloy tube type permeator used.



(a) (b)

Figure 5. Scanning electron microscope images of a V53-Ti26-Ni21 alloy (a) back-scattered and (b) secondary electron image.

Prototype Construction

The prototype was designed and fabricated consistent with ASME VIII considerations. The membrane was supported by a perforated metal substructure and was originally intended to be electron beam welded into the pressure boundary. Due to thermal strain mismatch and the desire to weld the membrane without filler metal, this fabrication approach resulted in numerous membrane failures. Consequently, a decision was made to braze the membrane into place using vacuum furnace brazing with BAu-4, a gold based braze alloy. As indicated previously, the braze processes caused significant rumpling of the membrane, as shown in Figure 2. In addition, two membrane repairs, as indicated by the arrows, are shown for this particular membrane, which was not tested. These repairs were made to the membrane due to the presence of solidification porosity in the ingot that was not healed during the HIP process.

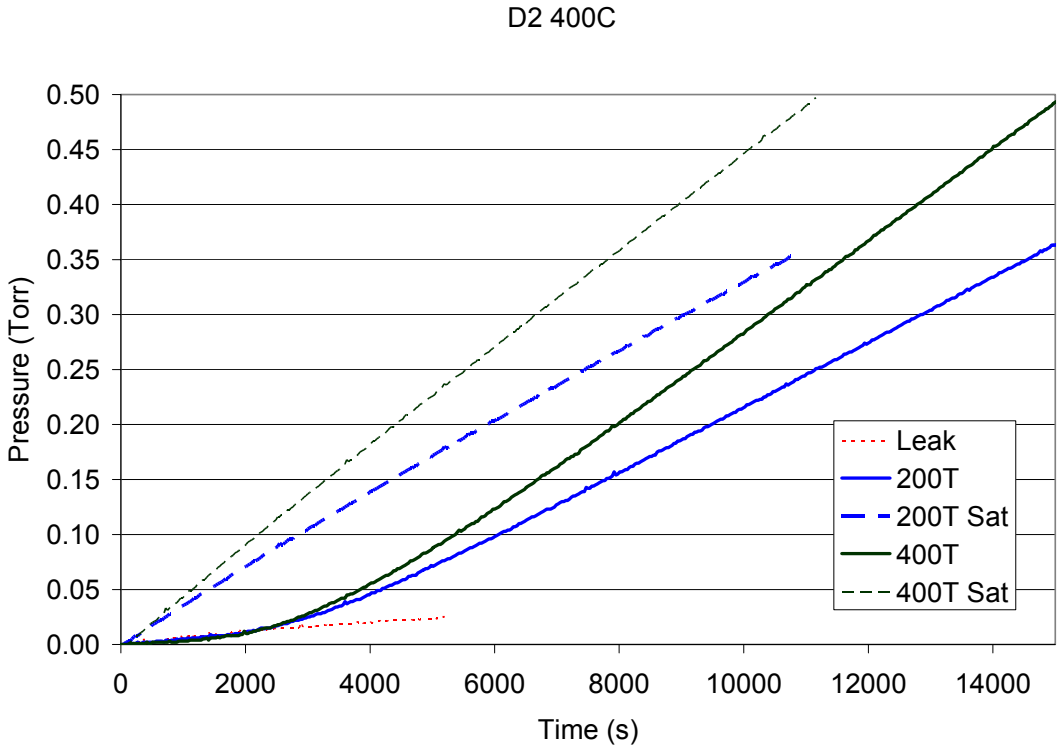


Figure 5. Pressure rise permeation testing of an early V51-Ti28-Ni21 membrane.

Subsequent to the brazing, the braze joint was visually inspected and subjected to leak testing. After these steps, the pressure boundary cover was welded onto the base using autogenous welding. This cover was also leak tested. The prototype was then installed in the permeation rack using flexible 6 mm stainless steel tubing; three thermocouples were attached to one surface. Simple heating tape with a 500°C limit was wrapped around the vessel. A variac and an overtemperature controller were used to supply power and protection, respectively.

Prototype testing

After assembly of the prototype into the permeation rack, Figure 6, the system was evacuated to below 1x10-6 Torr at room temperature and then baked out at approximately 100°C for 16 hours. The prototype was heated to a nominal temperature of 350°C. The system was continuously pumped on the low pressure side and a unit resolution mass spectrometer was used to monitor the break-through and equilibrium conditions.

A test pressure of 400 Torr was applied to the permeator and the hydrogen, helium, and total pressures were monitored with the mass spectrometer. In addition, the test chamber pressure was monitored using a Pirani gauge and the turbopump pressure was measured using a cold cathode ionization gauge. The various pressures and measured temperature are shown in Figure 7. There was a delay of approximately 1500 seconds for the hydrogen to break through the membrane. This delay can be used to estimate a diffusivity of 7×10^{-8} cm^2/s. Based on the pressure rise curves, the system had not achieved steady state at approximately 8400 seconds at which time an anomaly is observed in the data. The test was subsequently terminated.

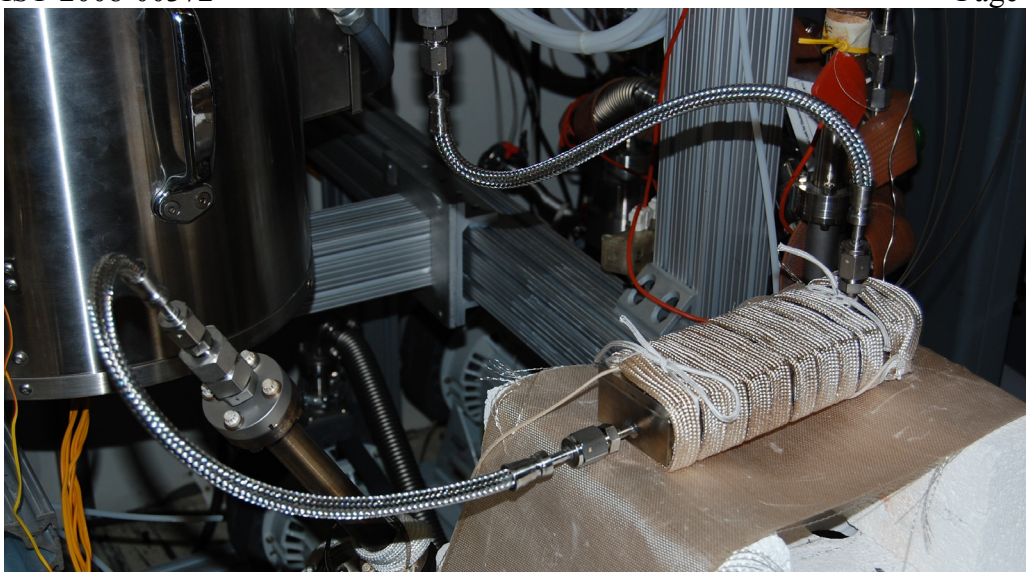


Figure 6. Wrapped and installed prototype permeator.

Upon cooling to room temperature, a helium leak test was conducted and a direct path between the pressure and vacuum sides of the membrane was detected. This membrane reactor in the installed configuration lasted only a few hours. Additional efforts to understand the failure mode will be undertaken. Several installation, testing, and operating conditions may have contributed to the short life of the reactor. This failure after such a short exposure time was certainly unexpected since previous tests had lasted tens of hours without membrane failure.

Summary and Conclusions

Vanadium Nickel Titanium alloys have been shown to have permeability values within an order of magnitude of Pd alloys.

Small disk samples were readily weldable using electron beam welding. However, when the membrane was scaled up to dimensions consistent with what would be required for a prototype, residual stresses and cooling stresses promoted cracking.

Vacuum furnace brazing was suitable for both braze repairing voids and pores in the membrane as well as for attaching the membrane to the pressure boundary structures.

The simple 5% scale prototype demonstrated and ability to pass hydrogen gas but failed after only 2.3 hours of exposure. The cause of the failure and resulting design modifications are underway for the next phase of prototype testing.

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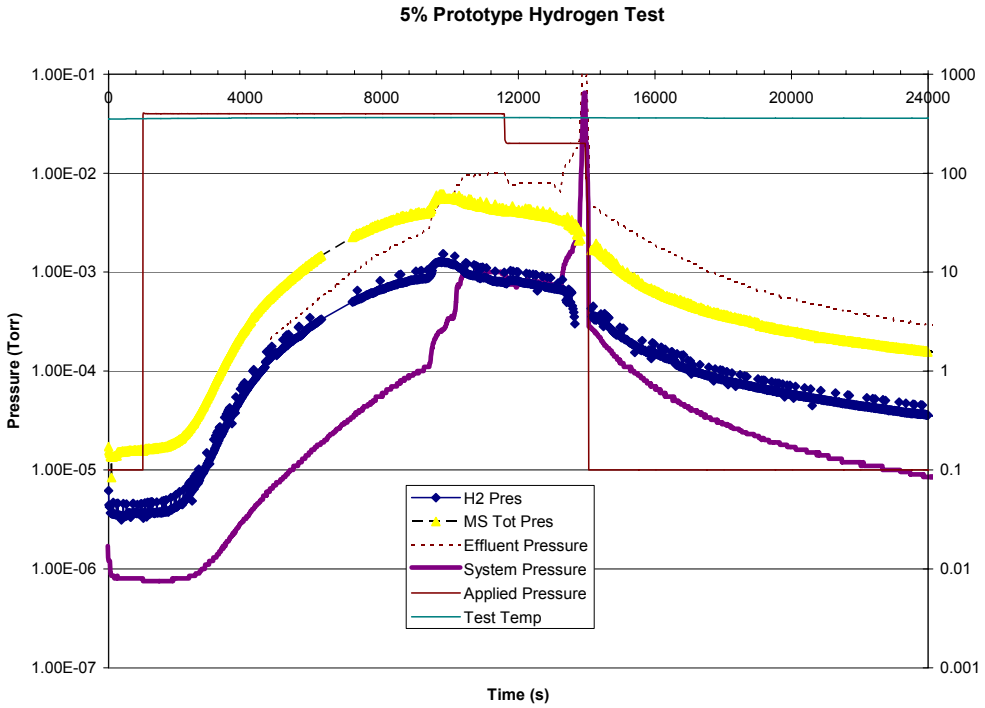

Figure 7. Dynamic permeation test results from the 5% scale permeator.

References

1. R. E. Buxbaum and T. L. Marker, Journal of Membrane Science, 85, 29-38, (1993).

2. N. M. Peachey, R. C. Snow, and R. C. Dye, Journal of Membrane Science, 111, 123-133, (1996).

3. T. S. Moss,N. M. Peachey, R. C. Snow, and R. C. Dye, International Journal of Hydrogen Energy, 23, 99-106, (1998)

4. C. Nishimura, M. Komaki, S. Hwang, and M, Amano, Journal of Alloys and Compounds, 330-332, 902-906, (2002).

5. Y. Zhang, T. Ozaki, M. Komaki, and C. Nishimura, Scripta Materialia, 47, 601-606, (2002).

6. K. Hashi, K. Ishikawa, T. Matsuda, and K. Aoki, Journal of Alloys and Compounds, 368, 215-220, (2004).

7. K. Hashi, K. Ishikawa, T. Matsuda, and K. Aoki, Journal of Alloys and Compounds, 404-406, 273-278, (2005).

8. Recent Progress of Zr-Based Bulk Amorphous Alloys, A, Inoue, Sci. Rep. RITU, A42, (1996) 1-11, No. 1, March 1996.